Precipitation of water from aqueous mixtures with addition of hydrophilic ions

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We examine phase separation in aqueous mixtures at fixed amounts of hydrophilic monovalent ions. When water is the minority component, preferential solvation can stabilize water domains enriched with ions. This ion-induced precipitation occurs in wide ranges of the temperature and the average composition where the solvent would be in one-phase states without ions. The volume fraction of such water domains is decreased to zero as the interaction parameter χ (dependent on the temperature) is decreased toward a critical value for each average composition.

In fluid mixtures containing water, phase separation behavior can be drastically changed by a small amount of a salt [1]. More strikingly, many groups have observed long-lived heterogeneities (sometimes extending over a few micrometers) in one-phase states [2] and a third phase visible as a thin plate at a liquid-liquid interface in two-phase states [3]. Very recently, mesophases with lamellar or onion structures have been found for an antagonistic salt composed of hydrophilic and hydrophobic ions [4]. Dramatic ion effects are ubiquitous in various soft matters. For example, in polyelectrolytes, the phase behavior sensitively depend on the degree of ionization and the composition for mixture solvents [5] and large-scale heterogeneities have been observed [6]. In these phenomena, the solvation interaction among ions and polar molecules should play a major role together with the Coulomb interaction among charges [7]. Recently some theoretical efforts have been made to elucidate the solvation effects in phase transitions in electrolytes and polyelectrolytes [8–10]. In this Letter, we consider hydrophilic monovalent ion pairs such as Na$^+$ and Cl$^-$ in a binary mixture of water and a less polar component (oil or alcohol) and examine ion-induced precipitation.

Neglecting the electrostatic interaction but accounting for the solvation interaction, we first consider a binary mixture in a cell with a fixed volume V. Here ions constitute the third component with density $n(\boldsymbol{r})$. The volume fractions of water, oil, and ions are written as $\phi(\boldsymbol{r})$ and $\phi'(\boldsymbol{r})$, and $v_I n(\boldsymbol{r})$, respectively, where v_I is the ionic volume. If the two solvent species have the same molecular volume v_0, their densities are ϕ/v_0 and ϕ'/v_0. The space-filling condition reads $\phi + \phi' + v_I n = 1$. The ion volume fraction is assumed to be small or $v_I n \ll 1$, which is easily satisfied for small ions with $v_I \ll v_0$. In this Letter we thus set $\phi' = 1 - \phi$, which simplifies the calculations.

When the ions have a strong preference of water over oil, we set up the free energy as

$$\frac{F}{T} = \int d\boldsymbol{r} \left[\frac{f(\phi)}{T} + \frac{C}{2} |\nabla \phi|^2 + n \ln(n v_0) - g n \phi \right], \quad (1)$$

where C is a positive constant and g is a positive parameter representing the ion preference of water. The space integral is within the cell. The Boltzmann constant will

be set equal to unity and then the temperature T represents the thermal energy of a particle. The free energy density $f(\phi)$ is taken to be the simple form,

$$v_0 f/T = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi), \quad (2)$$

where χ is the interaction parameter dependent on T and its mean-field critical value is 2 without ions. We fix the total particle numbers of the three components as

$$\bar{n} = \int d\boldsymbol{r} n / V, \quad \bar{\phi} = \int d\boldsymbol{r} \phi / V, \quad (3)$$

In equilibrium the homogeneity of the ion chemical potential $\delta F/\delta n$ yields

$$n = \bar{n} e^{g\phi} / \langle e^{g\phi} \rangle, \quad (4)$$

where $\langle e^{g\phi} \rangle = \int d\boldsymbol{r} e^{g\phi} / V$ is the space average of $e^{g\phi}$. Substitution of Eq.(4) into F in Eq.(1) gives

$$\frac{F}{T} = \int d\boldsymbol{r} \left[\frac{f(\phi)}{T} + \frac{C}{2} |\nabla \phi|^2 \right] + V \bar{n} \ln[\bar{n} v_0 / \langle e^{g\phi} \rangle]. \quad (5)$$

In equilibrium the chemical potential difference $h = \delta F/\delta \phi$ for the composition is also homogeneous. Here,

$$h = f'(\phi) - T C \nabla^2 \phi - T g n \quad (6)$$

where $f' = \partial f / \partial \phi$. Around a planar interface varying along the z axis, we obtain $T C (d\phi/dz)^2 = 2H(\phi)$, where

$$H(\phi) = f(\phi) - f(\phi_\alpha) - T(n - n_\alpha) - h(\phi - \phi_\alpha). \quad (7)$$

We suppose coexistence of a water-rich phase α and an oil-rich phase β with $\Delta\phi = \phi_\alpha - \phi_\beta > 0$. The compositions and the ion densities in the two phases are written as ϕ_α, ϕ_β, n_α, and n_β, respectively. The volume fraction of the phase α is denoted by γ_α. Since that of the phase β is $\gamma_\beta = 1 - \gamma_\alpha$, we have

$$\gamma_\alpha = (\bar{\phi} - \phi_\beta)/\Delta\phi = (\bar{n} - n_\beta)/\Delta n, \quad (8)$$

where $\Delta n = n_\alpha - n_\beta$. From Eq.(4) the ratio of the bulk ion densities is written as $n_\alpha/n_\beta = \exp(g\Delta\phi) \gg 1$ from

Eq.(4), where we assume $g\Delta\phi \gg 1$. Neglecting the surface free energy, we express F as

$$\frac{F}{V} = \gamma_\alpha f_\alpha + \gamma_\beta f_\beta - T\bar{n}\log[(\gamma_\alpha e^{g\phi_\alpha} + \gamma_\beta e^{g\phi_\beta})/\bar{n}v_0], \quad (9)$$

where $f_\alpha = f(\phi_\alpha)$ and $f_\beta = f(\phi_\beta)$. We minimize this F with respect to γ_α, ϕ_α, and ϕ_β at fixed $\bar{\phi}$ to obtain

$$h = f'_\alpha - Tgn_\alpha = f'_\beta - Tgn_\beta, \quad (10)$$
$$f_\alpha - f_\beta - T\Delta n = h\Delta\phi, \quad (11)$$

where $f'_\alpha = f'(\phi_\alpha)$ and $f'_\beta = f'(\phi_\beta)$. These equations also follow from Eqs.(6) and (7).
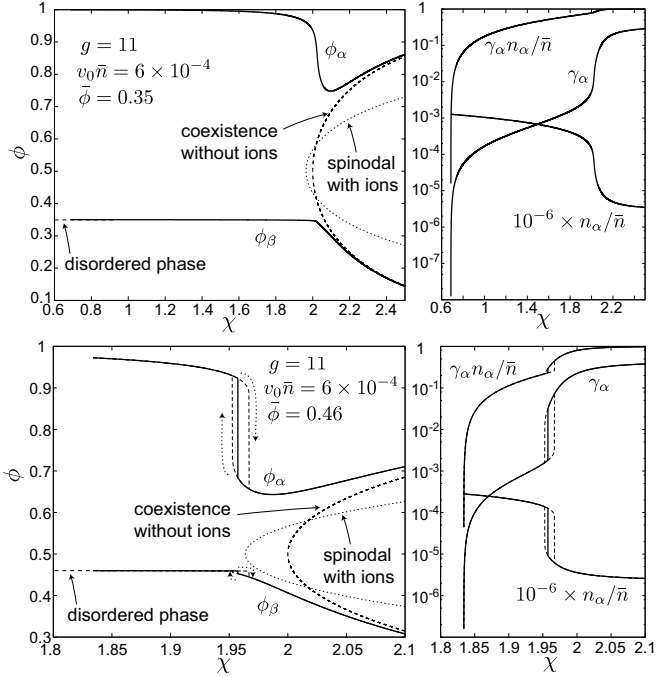

FIG. 1: Compositions ϕ_α and ϕ_β (left) and γ_α, $\gamma_\alpha n_\alpha/\bar{n}$, and $n_\alpha/\bar{n}$ (right) vs χ, where $\bar{n} = 6 \times 10^{-4}v_0^{-1}$ and $g = 11$. For $\bar{\phi} = 0.35$ (top), ϕ_α continuously changes for $\chi > \chi_{\rm p} = 0.687$. For $\bar{\phi} = 0.46$ (bottom), ϕ_α jumps at $\chi \cong 2$, where $\chi_{\rm p} = 1.834$. Shown also are the coexistence curve without ions and the spinodal curve with ions. The latter follows from a shift of the spinodal curve without ions by $g^2v_0\bar{n}/2$ to the left [8].

Our main finding is that there appears a precipitation branch of $\phi = \phi_\alpha \cong 1$ in the region $\chi < 2$ for $g \gg 1$. In Eq.(10) we set $f'_\alpha \cong v_0^{-1}T[-\log(1-\phi_\alpha)-\chi]$ to obtain

$$1 - \phi_\alpha \cong A_\alpha \exp[-gG(\phi_\beta)], \quad (12)$$

where $A_\alpha = \exp(\chi + v_0 f'_\beta/T)$. Here we introduce

$$\begin{aligned} G(\phi) &= -v_0[f(\phi) + (1-\phi)f'(\phi)]/T \\ &= -\log\phi - \chi(1-\phi)^2, \end{aligned} \quad (13)$$

where the second line follows from Eq.(2). By setting $f_\alpha \cong 0$ in Eq.(11) we also find $v_0n_\alpha = G(\phi_\beta)$. Outside the spinodal curve without ions, we notice $dG/d\phi =$
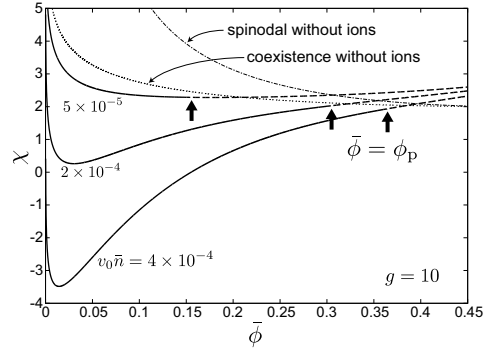

FIG. 2: $\chi = \chi_{\rm p}(\bar{\phi})$ for $v_0\bar{n} = 4\times10^{-4}$, 2×10^{-4}, and 5×10^{-5}. Precipitation occurs for $\bar{\phi} < \phi_{\rm p}$ (arrows). Shown also are the coexistence and spinodal curves without ions.

$-v_0(1-\phi)\partial^2 f/\partial\phi^2 < 0$, which leads to $G(\phi) > 0$ from $G(1) = 0$. Thus the right hand side of Eq.(12) is small or $\phi_\alpha \cong 1$ for large g. The equation for ϕ_β is given by

$$v_0n_\alpha = G(\phi_\beta) = v_0\bar{n}\Delta\phi/[\bar{\phi} - \phi_\beta + e^{-g\Delta\phi}\Delta\phi] \quad (14)$$

where we may set $\Delta\phi \cong 1 - \phi_\beta$. As $\gamma_\alpha = (\bar{\phi} - \phi_\beta)/\Delta\phi$ decreases to zero, ϕ_β and n_α increase up to $\bar{\phi}$ and $v_0\bar{n}e^{g(1-\bar{\phi})}$, respectively. Remakably, ϕ_α and ϕ_β depend on $\bar{\phi}$. From the second line of Eq.(13), the precipitation branch exists only for $\chi > \chi_{\rm p}(\bar{\phi})$. The lower bound is

$$\chi_{\rm p} = [-\log(1-\bar{\phi}) - v_0\bar{n}e^{g(1-\bar{\phi})}]/(1-\bar{\phi})^2, \quad (15)$$

where $\gamma_\alpha \to 0$ as $\chi \to \chi_{\rm p}$.

To easily understand the mathematics, let us focus on the case $\gamma_\alpha \ll 1$, where $f_\alpha \cong 0$ and $f_\beta \cong f(\bar{\phi}) - f'_\beta(1-\bar{\phi})\gamma_\alpha$ in Eq.(9). Treating γ_α as an order parameter, we write the deviation $\Delta F = F(\gamma_\alpha) - F(0)$ of the free energy from the one-phase value $F(0)$ as

$$\Delta F/TV \cong A_1\gamma_\alpha - \bar{n}\log(1 + B_1\gamma_\alpha), \quad (16)$$

where $A_1 = v_0^{-1}G(\bar{\phi}) + \bar{n}g(1-\bar{\phi})$ and $B_1 = e^{g\Delta\phi} - 1 \cong e^{g\Delta\phi}$. For $w \equiv \bar{n}B_1/A_1 > 1$, ΔF has a negative minimum given by $-TVA_1(w\log w - w + 1)/B_1 < 0$ attained at

$$\gamma_\alpha = (w-1)/B_1 \cong v_0\bar{n}/G(\bar{\phi}) - e^{-g(1-\bar{\phi})}, \quad (17)$$

which is consistent with Eq.(14) in the limit $\phi_\beta \to \bar{\phi}$. The condition $w > 1$ is equivalent to $\chi > \chi_{\rm p}$ for $g \gg 1$.

Figure 1 gives the phase diagrams in the ϕ-χ plane with $\bar{n} = 6 \times 10^{-4}v_0^{-1}$ and $g = 11$. In the first case of $\bar{\phi} = 0.35$, ϕ_α changes continuously and is minimum at $\chi = 2.05$, where $\chi_{\rm p} = 0.687$ and the maximum of n_α is $0.381v_0^{-1}$ at $\chi = \chi_{\rm p}$. In the second case of $\bar{\phi} = 0.46$, where $\chi_{\rm p} = 1.834$ and $n_\alpha = 0.0842v_0^{-1}$ at $\chi = \chi_{\rm p}$, we find that ϕ_α changes discontinuously along a hysteresis loop in the range $1.953 < \chi < 1.967$. In equilibrium, F is minimized and the resultant discontinuous transition

is at $\chi = 1.957$. In Fig.2, we display curves of $\chi = \chi_{\mathrm{P}}(\bar{\phi})$ for three values of $\bar{n}$ with $g = 10$. Each curve assumes a minimum at small $\bar{\phi}$ far away from the coexistence curve without ions. With increasing $\bar{\phi}$, the precipitation branch shrinks and disappears as $\bar{\phi} \to \phi_{\mathrm{P}}$, where ϕ_{P} is a critical composition less than 0.5. As functions of $\bar{\phi}$ and χ, we show γ_α in Fig.3 in the continuous case of $g = 10$ and ϕ_α in Fig.4 in the discontinuous case of $g = 11$.

Without the electrostatic interaction, the surface tension of our system is expressed as the integral $\sigma = \int dz CT (d\phi/dz)^2$ around an interface varying along the z axis [8]. Use of Eq.(7) gives

$$\sigma = (2CT)^{1/2} \int_{\phi_\beta}^{\phi_\alpha} d\phi H(\phi)^{1/2}, \qquad (18)$$

where C is assumed to be a constant. In Fig.5, we display the function $[2H(\phi)v_0/T]^{1/2}$ for $g = 11$. Here $H(\phi) \cong f''(\phi_\beta)(\phi - \phi_\beta)^2/2$ as $\phi \to \phi_\beta$ with $f'' = d^2f/d\phi^2$. Thus we obtain $\sigma \sim TC(\Delta\phi)^2/2\xi$, where $\xi = (f''/CT)^{-1/2}$ is the correlation length at $\phi = \phi_\beta \cong \bar{\phi}$.
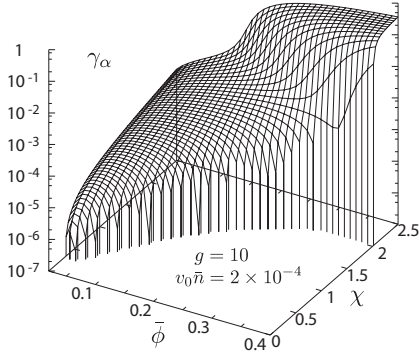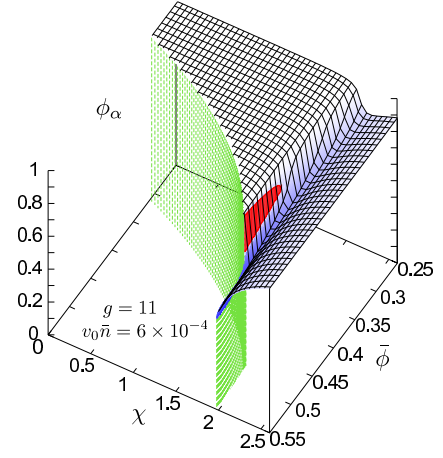

FIG. 4: (Color on line) Composition of the water-rich phase ϕ_α for $v_0\bar{n} = 6\times10^{-4}$ and $g = 11$. In this case a discontinuous transition occurs for $\chi \cong 1.95$ and $\bar{\phi} > 0.395$ (in red). One-phase states are realized for $\chi < \chi_{\mathrm{P}}$ or for $\bar{\phi} > \phi_{\mathrm{P}} = 0.473$ and $\chi < 2$ (in white). For $\chi > 2$, ϕ_α is little affected by ions.
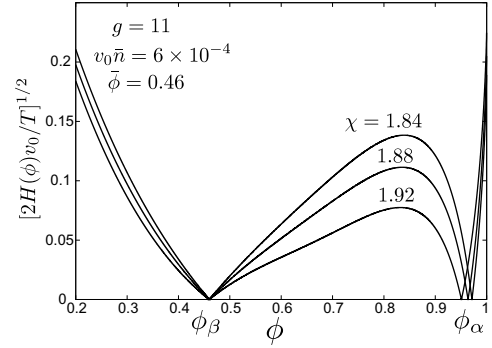

FIG. 3: Volume fraction of the water-rich phase γ_α as a function of χ and $\bar{\phi}$. for $\bar{n} = 2\times10^{-4}v_0^{-1}$ and $g = 10$. In this case γ_α decreases continuously to zero as $\chi \to \chi_{\mathrm{P}}$.

FIG. 5: $[2H(\phi)v_0/T]^{1/2}$ vs ϕ, vanishing at $\phi = \phi_\alpha$ and ϕ_β, where $\bar{\phi} = 0.46$, $\bar{n} = 6\times10^{-4}v_0^{-1}$, and $g = 11$.

Including the electrostatic interaction, we next consider aqueous mixtures containing a hydrophilic monovalent salt. The cation and anion densities are written as n_1 and n_2, whose total amounts are fixed as

$$\int d\mathbf{r}\, n_1 = \int d\mathbf{r}\, n_2 = V\bar{n}/2. \qquad (19)$$

The electric potential Φ satisfies the Poisson equation $\nabla \cdot \varepsilon\nabla\Phi = -4\pi e(n_1 - n_2)$, where the dielectric constant $\varepsilon(\phi)$ can depend on ϕ. The free energy F reads [8]

$$\frac{F}{T} = \int d\mathbf{r}\left[\frac{f(\phi)}{T} + \frac{C}{2}|\nabla\phi|^2 + \frac{\varepsilon|\nabla\Phi|^2}{8\pi T}\right.$$
$$\left. + \sum_{i=1,2}[n_i\ln(n_iv_0) - g_in_i\phi]\right]. \qquad (20)$$

The ion chemical potentials due to solvation, written as $\mu_{\mathrm{sol}}^i(\phi)$, strongly depend on ϕ. The interaction terms

($\propto g_i$) in F follow for the linear forms $\mu_{\mathrm{sol}}^i(\phi) = \mu_0^i - Tg_i\phi$ (where the first terms are irrelevant constants). This linear dependence is adopted to gain the physical consequences in the simplest manner. For each ion species i, the solvation-chemical-potential difference between the two phases is given by $\Delta\mu_{\alpha\beta}^i = Tg_i\Delta\phi$, which is the Gibbs transfer free energy in electrochemistry [11]. In aqueous solutions, $g_i \gg 1$ for hydrophilic small ions, while $g_i < 0$ for hydrophobic ions [8, 11]. We minimize F with respect to n_i under Eq.(19) to obtain

$$n_i = n_i^0 \exp[g_i\phi \mp e\Phi/T], \qquad (21)$$

where $-$ is for $i = 1$, $+$ is for $i = 2$, and $n_i^0 = \bar{n}/[2\int d\mathbf{r}\exp(g_i\phi \mp e\Phi/T)]$. The composition profile is determined by the homogeneity of $\delta F/\delta\phi$. Here we neglect the image interaction, whose role is reduced compared to that of the solvation interaction for not small ion densities [8, 12].

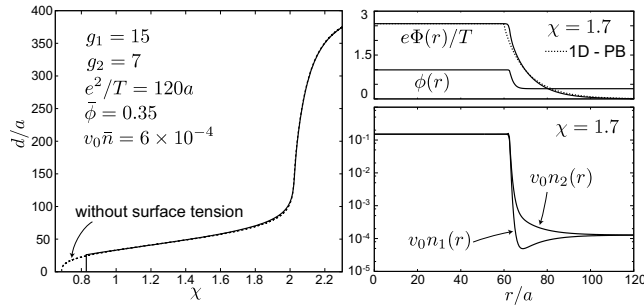For $g_1 = g_2 = g$, we have $n_1 = n_2 = n/2$ and $\Phi = 0$,

FIG. 6: Left: Numerical droplet radius d/a vs χ (bold line) together with the theoretical curve without the surface free energy (dotted line). Right: Normalized potential $e\Phi(r)/T$ and water volume fraction $\phi(r)$ (top), and normalized ion densities $v_0 n_1(r)$ and $v_0 n_2(r)$ (bottom), where $\chi = 1.7$. Here $g_1 = 15$, $g_2 = 7$, $\bar\phi = 0.35$, and $v_0\bar n = 6 \times 10^{-4}$.

so F in Eq.(20) reduces to F in Eq.(1). For $g_1 \neq g_2$, an electric double layer appears at the interface with a potential difference $\Delta\Phi = T(g_1 - g_2)\Delta\phi/2e$ across it, but the bulk phase relations (10) and (11) still hold with

$$g = (g_1 + g_2)/2. \qquad (22)$$

In Fig.6, we give numerical results for $g_1 = 15$, $g_2 = 7$, $\bar\phi = 0.35$, and $v_0\bar n = 6\times10^{-4}$. The space unit is $a = v_0^{1/3}$. We suppose a spherical water-rich droplet with radius d placed at the center of a spherical cell with radius $R = 600a$. Then $\gamma_\alpha = (d/R)^3$. The dielectric constant is of the form $\varepsilon = 40(1 + \phi)$. We also set $aC = \chi$ and $e^2/T = 120a$. In the left, the droplet disappears at $d = 26.0a$, where w in Eq.(17) is 1.08. This critical radius follows if the bulk free energy ΔF in Eq.(9) is equated with the minuns of the surface free energy $4\pi\sigma d^2$. In the right, we

set $\chi = 1.7$ to display the profiles of $\Phi(r)$, $\phi(r)$, $n_1(r)$, and $n_2(r)$. We obtain $\phi_\alpha = 0.993$ and $n_\alpha = 0.352v_0^{-1}$ within the droplet and $\phi_\beta = 0.349$ and $n_\beta = 2.55 \times 10^{-4}v_0^{-1}$ outside it. In Fig.6, the potential $\Phi(r)$ relaxes with the Debye length $\kappa_\beta^{-1} = 11.8a$ and is well fitted to the one-dimensional solution of the nonlinear Poisson-Boltzmann equation (dotted line) with $\Delta\Phi = 3T/e$ [8]. Here n_α and n_β are the bulk values of $n = n_1 + n_2$.

In future we should explain the experimental findings of large-scale heterogeneities [2]. We note that one-phase states are metastable outside the spinodal curve with ions ($\chi < 1/2\bar\phi(1-\bar\phi) - g^2 v_0\bar n/2$) in Fig.1. Thus precipitation from a one-phase state should be triggered by some impurities and/or hydrophilic walls. We also note that the wetting transition of aqueous mixtures is much influenced by the ion-induced precipitation mechanism.

Experiments are informative, where the temperature, the water volume fraction, and the salt amount are varied. We mention an experiment by Leunissen et al. [13], where micron-sized water droplets containing ions formed a crystal in an oil with low dielectric constant ($\varepsilon_{oil} = 4 - 10$) without a surfactant. Graaf et al. [14] ascribed its origin to the screened Coulomb interaction among droplets. We also propose experiments of the salting-out effect of polyelectrolytes in water-alcohol [5], where the degree of ionization much increases with accumulation of water around the polymers [10].

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